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19. ABSTRACT (Continued from Page 1)

Imidazolium, aralkylammonium and sulfonium chlorides were found to have high solubility and conductivity in thionyl chloride, but lithium was found to be passive in contact with these solutions and most metals corroded excessively. These salts mixed with aluminum chloride were much less aggressive and when mixed with lithium salts in addition gave high conductivity and test cell capacities. In finished cells, however, the solutions were still too corrosive to make stable systems.

New Liquid Cathode Electrolytes in High Rate Cells

Jean W. Bailey, David W. Kalisz and George E. Blomgren
Eveready Battery Company, Inc.
Westlake, Ohio 44145

Abstract

The power limitations of liquid oxyhalide batteries have been explored by examining the physical and electrical properties of new electrolytes. Conductivity, kinematic viscosity and specific gravity of electrolytes were measured inside a specially adapted argon filled drybox. Liquid cathode oxyhalide electrolytes designed to enhance power density were tested first in demountable test cells and then, the most promising, in hermetically sealed high rate F size jellyroll cells. For F cells, the capacity on constant current discharge was measured at 3.5 and 12.5 mA/cm² for fresh cells at 21°C and at 3.5 mA/cm² for cells stored 4 weeks at 54°C then discharged at -30°C. An optimized cell design with thicker electrodes was developed for testing electrolytes with higher conductivity than LiAlCl₄-SOCl₂. The best capacity at 2A was achieved with LiGaCl₄-SOCl₂ or LiAlCl₄-SOCl₂. The best capacity at 7A was achieved with LiGaCl₄-SOCl₂. LiGaCl₄ in SOCl₂ was found to discharge at higher temperatures than LiAlCl₄ in SOCl₂. Imidazolium, aralkylammonium and sulfonium chlorides were found to have high solubility and conductivity in thionyl chloride, but lithium was found to be passive in contact with these solutions and most metals corroded excessively. These salts mixed with aluminum chloride were much less aggressive and when mixed with lithium salts in addition gave high conductivity and test cell capacities. In finished cells, however, the solutions were still too corrosive to make stable systems.

Introduction

The object of this work is to characterize the factors which influence performance and to identify the best performing oxyhalide electrolyte for a high rate Li cell. A possible application of the high rate Li battery is to charge a capacitor or a surface charge effect battery in a short recycle time. The physical properties of new electrolytes were examined and the electrolytes were evaluated in demountable experimental test cells and then in hermetically sealed high rate F size Li-SOCl₂ cells. For the F cells, the capacity on constant current discharge was measured at 3.5 and 12.5 mA/cm² (2A and 7A respectively) for fresh cells at 21°C and at 3.5 mA/cm² for cells stored 4 weeks at 54°C then discharged at -30°C. The temperature during discharge was measured via a thermocouple taped to the outside of the cell at half height. The heat was also measured via microcalorimetry of small bobbin cells that fit into the microcalorimeter chamber.

The oxyhalides evaluated were SOCl₂ and SO₂Cl₂. The

electrolyte salts were various concentrations of LiAlCl_4 , LiGaCl_4 , methylethylimidazolium chloride (MEIC) 1:1 with AlCl_3 as a mixed salt electrolyte with LiAlCl_4 , trimethylphenylammonium chloride (TMPAC) or trimethylsulfonium chloride (TMSC) with AlCl_3 as a mixture with LiAlCl_4 and TMPAC in a 1:1 mixture with AlCl_3 . MEIC is a chlorobasic electrolyte with good conductivity in SOCl_2 . Unfortunately it proved to be extremely corrosive to stainless steel and nickel and severely passivating toward lithium, so it could be tested only by adding AlCl_3 in a 1:1 mole ratio to form a neutral electrolyte. LiGaCl_4 has been reported to have good high rate performance and conductivity equivalent to LiAlCl_4 .¹ MEIC, TMSC and TMPAC form room temperature molten salts with AlCl_3 ²⁻⁴ and it was hoped that the cations would be essentially unsolvated in the oxyhalide solvents and would thus have high mobility. S_2Cl_2 is a good solvent for sulfur and is a suspected intermediate in the discharge reaction of thionyl chloride.⁵ It was added to improve cathode performance at high rate.

Experimental

The LiAlCl_4 - SOCl_2 electrolytes were prepared by refluxing SOCl_2 (Mobay, 99.6%) containing AlCl_3 (Fluka, puriss. grade) and LiCl (Lithcoa or Alfa, anhydrous ultrapure) in 5% excess to insure neutralization of the AlCl_3 . The moisture content was monitored by measuring the infrared absorbance in a 1 cm path length quartz cell on a Perkin-Elmer 1320 infrared spectrophotometer. Refluxing was discontinued when there was no detectable absorbance at 3360 cm^{-1} , arising from the hydroxide ion complexed to aluminum, and the HCl absorbance at 2720 cm^{-1} was less than 0.045 absorbance units (<5 ppm).

Less concentrated electrolytes were prepared by dilution of 1.5 or 1.8M LiAlCl_4 - SOCl_2 with pure SOCl_2 . S_2Cl_2 (Alfa Products, ultrapure, 99.999%) was added directly to the electrolyte without purification. The moisture content of the electrolyte was checked after preparation. The mixed salt electrolyte with MEIC was prepared by adding .25 mole MEIC and .25 mole AlCl_3 to 1.25 mole LiAlCl_4 in 1 l SOCl_2 and refluxing again as required to remove moisture contamination. MEIC was synthesized in-house from chloroethane and 1-methylimidazole.² 1M MEIC (or TMPAC, TMSC) was prepared by refluxing MEIC in SOCl_2 and checking for moisture as described above. The mixed salt electrolyte in SO_2Cl_2 (Alfa Products, 99%) was prepared in the same way. The mixed salt electrolyte with TMSC (Stauffer Chemical), or TMPAC (Eastman Kodak), was prepared by adding 0.25 moles of TMSC (TMPAC) and 0.25 moles of AlCl_3 to 1.25 moles LiAlCl_4 in 1 l SOCl_2 and refluxing. The LiGaCl_4 - SOCl_2 electrolyte was prepared from LiGaCl_4 (Anderson Physics Labs) and SOCl_2 with refluxing to remove moisture.

Due to the corrosive nature and moisture sensitivity of



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oxyhalides, the measurement of physical properties required special adaptation of apparatus to work in an argon filled drybox with a dewpoint of -65°C or better. A Haake refrigerated bath and circulator model A 81 filled with Dow Corning 200 Silicone fluid, 5 cSt., was installed outside the drybox. The silicone fluid was circulated through the drybox wall and into a jacketed beaker containing the electrolyte. The temperature range was -18°C to 25°C . The Yellow Springs Instruments conductivity cell model 3403, $k=1.0/\text{cm}$ was connected via electrical feed through contacts to the conductivity bridge, Electro Scientific Industries Impedance Meter model 251, outside the drybox. The kinematic viscosities were measured inside the drybox using Cannon-Fenske type viscometers. The jacketed beaker arrangement was also used, but with silicone heat transfer fluid also inside the beaker to control the temperature of the electrolyte in the viscometer. The specific gravities were measured by setting up a Westphal density balance inside the drybox.

Preliminary cell tests were carried out in demountable cells constructed of blocks of TEFZEL which were milled to form a slot with limited access to electrolyte. The cell is described in detail elsewhere,⁶ but in our electrolyte studies we added an additional layer of separator and of lithium in order to have lithium on both sides of the cathode collector strip. The collector strip was obtained from the same stock used in making F cells and was slit to size and carbon removed from one end to secure a good contact with the central metal mesh.

Microcalorimetry measurements were made with a Tronac model 351RA. The small cylindrical bobbin cells used for microcalorimetry were described previously by Johnson et al.⁶ The F size cells used for electrolyte capacity evaluation were previously described by A.D. Ayers et al.⁷

Results and Discussion

Conductivity and viscosity were used as initial guides to promising electrolytes. The highest conductivities contribute the least solution resistance to the overall electrical impedance while the lowest viscosity should permit the minimum flow impedance occurring during discharge as the cathode swells with products and the anode contracts as lithium dissolves. Table 1 gives the results of conductivity, viscosity and density studies. It was surprising that the MEIC in SOCl_2 gave superior conductivity to LiAlCl_4 at the same concentration (1 M), but also that the solubility was so high. Previous work⁸ would suggest a very limited solubility of any ionic chloride in oxyhalide solvents. Clearly, the high polarizability of the cation plays a role in encouraging solubility. A similar high solubility was noted for TMPAC and TMSC in thionyl chloride, although conductivity was not measured for TMSC. The slightly lower

conductivity and higher viscosity for TMPAC compared to MEIC can be explained by the larger cation in TMPAC and higher viscosity. The series of studies of LiAlCl_4 at various concentrations in SOCl_2 shows good agreement, where results overlap, with the most recent studies in the literature of Berg et al,⁹ who point out the discrepancies with earlier literature. Our viscosity and density results agree with the measurements of Venkatesetty and Saathoff¹⁰ to within about $\pm 3\%$. We believe that our greater precaution with the solutions in handling in the dry box gave us more accurate results. A qualitative interpretation of these results in terms of dissociation of ion pairs at higher concentration was recently presented.¹¹ The mixed electrolyte solutions show slightly higher conductivity and lower viscosity for MEIC- AlCl_3 - LiAlCl_4 compared to 1.5 M LiAlCl_4 , while the corresponding solutions of TMPAC show lower conductivity with lower viscosity. The effect of the S_2Cl_2 additive is to lower the conductivity slightly, but the concentration is also lowered, which would be expected to cause a lowered conductivity. The higher molecular weight sulfur monochloride (compared to thionyl chloride) causes an increase in the solution viscosity under all conditions. The conductivity studies encouraged us to submit all of the electrolytes to cell tests.

Table 2 gives the results of the demountable cell tests for tests carried out at 10 mA/cm^2 . The results for 1 M TMPAC and MEIC solutions are not included because no capacity or even a stable open circuit voltage was obtained. The results clearly ruled out the low concentration 0.5 M LiAlCl_4 and the 1M TMPAC-1M $\text{AlCl}_3/\text{SOCl}_2$ solution because of the poor performance at the high rate. We believe that the latter solution performs poorly because of cathode passivation or polarization caused by precipitation of the voluminous TMPAC, as evidenced by the cathode to reference voltage which follows the cell polarization during discharge. The $\text{LiGaCl}_4/\text{SOCl}_2$ solution and the MEIC mixed electrolyte sulfuryl chloride solution gave superior results in this test. The other solutions gave similar results to within the margin of error, although the sulfur monochloride showed slightly better results on average than the other solutions. Further experimentation with MEIC and TMPAC showed that the lithium was passive and that either nickel or stainless steels dissolve rapidly in the electrolyte even when coupled to lithium. Molybdenum and tungsten did not dissolve in the electrolyte, but using either of these metals as lithium collector did not lead to the normal lithium potential. Instead, the potentials were very cathodic to lithium, an indication of the passivity of the lithium surface. Apparently, the high availability of chloride ion and the extreme insolubility of LiCl leads to immediate passivation of lithium in any of these chloride media. The tetrachloride salts do not give up the chloride ion so easily and so the source of the chloride must be the thionyl chloride as it undergoes reduction on the unfavorable lithium chloride surface on lithium. Because these results did not lead to definitive

results for many of the electrolytes, we carried the testing to further stages.

The heat output of cells with these electrolytes was measured in the microcalorimeter. Since F cells are too large to be accommodated in the chamber, small bobbin cells were evaluated. Table 3 gives the results. The lowest heat output was 26 μ watts obtained from the cells with LiGaCl_4 electrolyte. The greatest heat was 213 μ watts from 1.5 M $\text{LiAlCl}_4/\text{SO}_2\text{Cl}_2$, but sulfuryl chloride is known to cause more corrosion than thionyl chloride. The various concentrations of $\text{LiAlCl}_4\text{-SOCl}_2$ had 42 - 43 μ watts except for 1.3M at 64 μ watts. The reason for the difference is unknown, but considerable variability in heat evolution is common in the early stages of cell life, although the standard deviation of this set of cells was small. Since the cells were measured at different ages, we regard these results as semiquantitative only. The addition of S_2Cl_2 to 1.8M LiAlCl_4 was expected to increase corrosion and it did increase the heat output from 43 to 65 μ watts.

Table 4 gives F cell performance on the 2A test. Two cells from each lot were tested. The Student t-test from statistics shows that they fall into two groups with equivalent performance, as indicated. The temperature of the cells was recorded by a thermocouple taped to the outside of the cell at half height. It gave surprisingly reproducible results. The temperature at midlife for most of the cells was about 28°C. The exceptions were for LiGaCl_4 and SO_2Cl_2 . Figure 1 gives a typical plot of the heat generated during discharge at 2A. The temperature of the control cells with 1.5M $\text{LiAlCl}_4/\text{SOCl}_2$ increases about 6 degrees at the beginning and is constant throughout the plateau region of discharge. It increases again as the cell fails due to the increased internal resistance. A quite different temperature profile is seen with LiGaCl_4 . Instead of a plateau the temperature increases steadily during discharge. At 7A more heat is generated with both LiAlCl_4 and LiGaCl_4 as shown in Figure 2. Table 5 shows the cell temperatures at midlife for all the cells at both rates. The highest temperatures were measured from LiGaCl_4 cells. The next greatest heat was generated from $\text{LiAlCl}_4/\text{SO}_2\text{Cl}_2$ cells which had an average midlife temperature of 35 vs. 29 degrees for the equivalent SOCl_2 cells.

The capacities of the cells improve at elevated temperature. Cells from the same lot discharged at 54°C had 14.44 Ah compared to 12.88 Ah at 21°C, as shown in Table 6. The $\text{LiGaCl}_4/\text{SOCl}_2$ electrolyte cells ran at higher temperature than control, 1.5M $\text{LiAlCl}_4/\text{SOCl}_2$, at both rates. The capacity of LiGaCl_4 cells exceeded the control at the high rate, 7A, as shown in Table 7. and in the second evaluation of optimized cells at 2A which is discussed below. This capacity was equivalent to control in the first evaluation. The conductivity of LiGaCl_4 electrolyte¹ is 20 mS/cm at 25°C compared to 19.5 for control. The higher operating

temperature may be responsible for the improved capacity, since the small conductivity difference would not be expected to cause the capacity differences. The reason for the higher operating temperature is unknown, though it is not due to increased corrosion as demonstrated by the microcalorimetry measurements of heat output. This property may not be a benefit in all situations, however, since heat dissipation can be a major problem in battery configurations and in confined battery compartments. Safety problems frequently arise from such situations.

The performance on the 4 week 54°C, 2A at -30°C discharge test is shown in Table 8. During the 54°C shelf the cells with MEIC, TMPAC and TMSC leaked. Replicate cells also leaked. Because of the corrosion and leakage at the etched vent, further testing with these electrolytes was discontinued. The cell temperature during the low temperature test is also shown in Table 8. The higher operating temperature of the LiGaCl₄ salt is seen even on this -30°C test as shown in Figure 3.

The F cell used for the electrolyte evaluation to this point was the design from Eveready's military contract. The cell is technically Li limited but at the 2A rate it is effectively carbon limited. In order to find performance improvements with new electrolytes with better conductivity, it was desirable to shift the cell balance, remaining within carbon limitation, to achieve greater cathode capacity. This was done by making shorter, thicker electrodes which reduces the volume of inactive cell components such as carriers and separators. The penetration depth of the reaction in the cathode depends on conductivity so only an electrolyte of high conductivity will be able to take advantage of the increased capacity. The relationship between penetration depth and conductivity is described by the equations below. The penetration depth l^* is the depth of the electrode into which the majority of the reaction extends¹².

$$l^* = (RTk/nFi_0a)^{1/2} \quad (\text{linear polarization region})$$

$$l_T = kRT/I\alpha nF \quad (\text{Tafel polarization region})$$

where:

- i_0 is the exchange current density (A/cm²)
- k is the effective specific conductivity of the electrolyte (S/cm)
- a is the specific surface area (cm²/cm³)
- α is the transfer coefficient for the cathode reaction
- I is the cathodic current density (a/cm²)

The effective conductivity is defined by the relationship¹³:

$$k = k_0 V_1^t$$

where:

- k_0 is the specific conductivity in the bulk electrolyte phase (S/cm)
- V_i is the specific volume of phase i in the porous matrix (cm^3/cm^3)
- t is the tortuosity factor

Using data from Tsaur and Pollard¹³, we calculate for the Tafel region (since we are trying to optimize for high currents) at 1 mA/cm^2 , $l^T = 0.240 \text{ in. (0.6 cm)}$, at 5 MA/cm^2 , $0.047 \text{ in. (0.12 cm)}$, and for 10 mA/cm^2 , $0.024 \text{ in. (0.060 cm)}$, thus showing the need for very thin electrodes for high rate performance.

Based on the above penetration depth results, an empirical optimization for the F cell was developed to determine the best combination of anode and cathode thickness. A body of performance data from cells with different electrode lengths and thickness were used for the optimization. The optimization assumed that a cathode of a given thickness will have a capacity per unit length independent of the anode thickness. The capacity per cm vs cathode thickness at two current levels was plotted as shown in figure 4.

Although cathode utilization decreases with increasing thickness the proportion of the cell volume filled with inactive components also decreases with increasing electrode thickness. The optimum electrode thickness is determined by plotting the cathode length as a function of thickness of the total electrode stack as shown in figure 5. To optimize, an anode thickness is chosen and paired with the range of cathode thicknesses. For each cathode thickness the total stack thickness is calculated and from that the cathode length is determined from Figure 5. Next the cathode capacity in Ah/cm is determined from Figure 4 and multiplied by the cathode length. The anode length is always 7.4 cm shorter than the cathode so the anode length and theoretical capacity can be calculated. For each anode thickness there is a break point where the cell goes from carbon limitation to anode limitation as shown in figure 6 by the change from positive to negative slope in three cases. In these three cases the anode is thinner than 0.014 inches and anode limitation determines the optimum. For thicker anodes the optimum is out of the experimental range.

The control electrode combination is marked in Figure 6 as are the two experimental combinations selected for testing. As can be seen we have shifted to shorter, thicker electrodes, but stayed on the cathode limited side, positive slope, of each curve. The cells made with these electrodes were tested at 2A and 7A at 21°C. The results are given in Tables 9 and 10. Unfortunately, the optimized design did not result in a capacity improvement with the group of electrolytes tested because they do not have significantly better conductivity than control. The

MEIC- AlCl_3 electrolytes had better conductivity for their concentration but could not be tested because of the severe corrosion they caused. The conductivity of LiGaCl_4 was not sufficiently greater than control to show a difference. Thus, the best electrolyte for Li-oxyhalide cells is the standard electrolyte $\text{LiAlCl}_4\text{-SOCl}_2$ and $\text{LiGaCl}_4\text{-SOCl}_2$ particularly at high rates.

Summary and Conclusions

The best electrolytes for Li oxyhalide cells were found to be $\text{LiAlCl}_4\text{-SOCl}_2$ and $\text{LiGaCl}_4\text{-SOCl}_2$. An optimized cell design with thicker electrodes was developed for testing electrolytes with higher conductivity than $\text{LiAlCl}_4\text{-SOCl}_2$. Imidazolium, aralkylammonium and sulfonium chlorides form interesting solutions of high conductivity, but, because of their very aggressive nature, successful finished cells could not be made. It is possible, however, that reserve cell configuration or low temperature storage could be used to take advantage of the unusual properties of these salts when mixed with a Lewis acid salt like AlCl_3 and a lithium salt. Their use as sole salts is prohibited, however, by extreme lithium passivation.

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- Figure 1 Comparison of F cell capacity and heat output at 2A and 21°C. Electrolytes = 1.5M LiAlCl₄/SOCl₂ and 1.5M LiGaCl₄/SOCl₂
- Figure 2 Comparison of F cell capacity and heat output at 7A and 21°C. Electrolytes = 1.5M LiAlCl₄/SOCl₂ and 1.5M LiGaCl₄/SOCl₂
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- Figure 4 F cell capacity as a function of cathode thickness at 2A and 750 mA discharge currents.
- Figure 5 F cell cathode length as a function of total electrode stack thickness.
- Figure 6 Calculated F cell capacity as a function of cathode thickness with different anode thickness. Electrode lengths chosen to fill available cell volume.

Table 1
Physical Properties of Various Solutions as a Function of Temperature
[Conductivity, k (S/cm); Viscosity, η (cP); and Density, d (g/cm³)]

Temperature (°C)	1.00 M NEIC/ SOCl_2			1.00 M THPAC/ SOCl_2			0.25 M NEIC+ AlCl_3 in 1.25 M LiAlCl_4 / SOCl_2			0.25 M THPAC+ AlCl_3 in 1.25 M LiAlCl_4 / SOCl_2		
	k	η	d	k	η	d	k	η	d	k	η	d
25	16.44	1.254	1.6090	13.73	1.322	1.5983	20.00	1.670	1.6666	18.80	1.704	1.6694
20	15.56	1.322	1.6158	13.35	1.375	1.5955	19.62	1.808	1.6750	18.19	1.850	1.6770
15	14.79	1.400	1.6245	12.45	1.518	1.6030	18.90	1.964	1.6830	17.30	2.022	1.6852
10	13.84	1.521	1.6310	11.72	1.606	1.6090	18.010	2.140	1.6903	16.88	2.208	1.6930
5	13.01	1.631	1.6400	11.01	1.764	1.6173	17.22	2.333	1.6973	16.16	2.418	1.7009
0	12.08	1.786	1.6475	10.16	1.919	1.6260	16.28	2.635	1.7075	15.21	2.674	1.7100
-5	11.30	1.948	1.6545	9.37	2.085	1.6318	15.20	2.859	1.7136	14.26	2.914	1.7180
-10	10.28	2.162	1.6625	8.98	2.301	1.6380	14.15	3.211	1.7245	13.25	3.332	1.7205
-15	9.40	2.391	1.6702	8.11	2.510*	1.6452*	12.90	3.642	1.7325	12.10	3.742	1.7340
* data at 14° C												
	1.5 M LiAlCl_4 / SOCl_2 with 59 S_2Cl_2			1.5 M LiAlCl_4 / SOCl_2 with 189 S_2Cl_2			0.5 M LiAlCl_4 / SOCl_2			1.0 M LiAlCl_4 / SOCl_2		
	k	η	d	k	η	d	k	η	d	k	η	d
25	18.50	1.780	1.6918	15.14	1.815	1.6908	7.59	0.887	1.6540	15.42	1.259	1.6760
20	18.20	1.931	1.6995	14.88	1.979	1.6970	7.58	0.952	1.6625	15.24	1.342	1.6826
15	17.60	2.112	1.7053	14.25	2.138	1.7022	7.56	1.012	1.6710	14.86	1.446	1.6904
10	17.00	2.287	1.7110	13.57	2.345	1.7140	7.52	1.070	1.6786	14.43	1.602	1.6990
5	16.18	2.530	1.7235	12.98	2.558	1.7210	7.42	1.160	1.6895	13.96	1.733	1.7075
0	15.15	2.788	1.7300	12.24	2.838	1.7283	7.30	1.237	1.6980	13.42	1.854	1.7160
-5	14.15	3.125	1.7380	11.40	3.160	1.7373	7.20	1.347	1.7055	12.80	2.029	1.7240
-10	13.05	3.572	1.7450	10.60	3.562	1.7446	7.00	1.469	1.7155	12.07	2.260	1.7316
-15	11.71	—	—	9.68	3.987	1.7520	6.70	1.602	1.7245	11.35	2.493	1.7400
	1.5 M LiAlCl_4 / SOCl_2			1.8 M LiAlCl_4 / SOCl_2			2.0 M LiAlCl_4 / SOCl_2					
	k	η	d	k	η	d	k	η	d	k	η	d
25	19.58	1.746	1.6920	21.40	2.167	1.6983	20.20	4.244	1.7124			
20	19.20	1.895	1.6976	20.40	2.336	1.7043	18.95	4.776	1.7194			
15	18.20	2.063	1.7060	19.46	2.532	1.7120	17.90	5.318	1.7268			
10	17.68	2.238	1.7140	18.60	2.800	1.7202	16.68	5.981	1.7320			
5	16.70	2.474	1.7230	17.78	3.163	1.7285	15.18	6.804	1.7390			
0	15.70	1.784	1.7310	16.73	3.854	1.7360	13.50	7.835	1.7476			
-5	14.87	3.080	1.7385	15.35	4.034	1.7446	12.05	9.134	1.7554			
-10	13.85	3.482	1.7455	14.10	4.471	1.7520	10.30	10.854	1.7610			
-15	12.70	3.937	1.7535	12.71	5.099	1.7605	8.70	12.621	1.7683			

Table 2

Demountable Test Cell Results at 10 mA/cm²

<u>Electrolyte</u>	<u>Current (mA)</u>	<u>Capacity (mAh)</u>	<u>Energy (mWh)</u>
0.5M LiAlCl ₄ /SOCl ₂	56.5 ±0.2	43 ±2	134 ±8
1.5M LiAlCl ₄ /SOCl ₂	58.4 ±0.6	106 ±2	339 ±7
1.8M LiAlCl ₄ /SOCl ₂	57.6 ±0.7	102 ±4	321 ±14
3.0M LiAlCl ₄ /SOCl ₂	58.2 ±0.4	103 ±4	331 ±15
1.25M LiAlCl ₄ /SOCl ₂ +0.25M (MEIC+AlCl ₃)	57.3 ±1.1	98 ±15	311 ±20
1.25M LiAlCl ₄ /SOCl ₂ +0.25M(TMPAC+AlCl ₃)	57.4 ±1.0	94 ±4	297 ±12
1.5 M LiAlCL ₄ /SOCl ₂ + 5% S ₂ Cl ₂	57.4 ±1.3	105 ±7	336 ±24
1.5M LiGaCl ₄ /SOCl ₂	59.8 ±1.1	123 ±11	405 ±36
1M TMPAC-1M AlCl ₃ / SOCl ₂	52.6 ±1.3	10 ±4	28 ±11
1.25M LiAlCl ₄ /SOCl ₂ +0.25M(TMSC+AlCl ₃)	56.4 ±1.6	72 ±8	227 ±25
1.25MLiAlCl ₄ /SO ₂ Cl ₂ +0.25M(MEIC+AlCl ₃)	54.4 ±1.3	121 ±6	363 ±18

Table 3

Heat Output of Bobbin Cells

<u>Electrolyte</u>	<u>Age at Test (days)</u>	<u>Number n</u>	<u>Heat μW</u>
1.0M LiAlCl ₄ /SOCl ₂	15	4	43 ± 3
1.3M LiAlCl ₄ /SOCl ₂	16	3	64 ± 2
1.5M LiAlCl ₄ /SOCl ₂	22	3	42 ± 11
1.8M LiAlCl ₄ /SOCl ₂	34	4	43 ± 14
1.8M LiAlCl ₄ /SOCl ₂ + 5% S ₂ Cl ₂	39	3	65 ± 11
1.5M LiGaCl ₄ /SOCl ₂	41	3	26 ± 8
1.5M LiAlCl ₄ /SO ₂ Cl ₂	50	4	213 ± 35

Table 4

Performance of F Cells with New Electrolytes

Test = 2A Constant Current, 21°C, fresh, 2 cells per lot.

Rank	Electrolyte	OCV	Voltage Delay to 2.7 V	CCV mid	Temp mid, °C	Cap Ah	En Wh
1.	1.5M LiAlCl ₄ /SOCl ₂	3.65	< 1 sec.	3.35	29.2	14.08 ±0.35	47.18 ±1.16
1.	1.5M LiGaCl ₄ /SOCl ₂	3.65	< 1 sec.	3.40	38.2	13.83 ±0.16	47.00 ±0.55
1.	1.8M LiAlCl ₄ /SOCl ₂	3.65	< 1 sec.	3.35	28.8	13.57 ±0.19	45.44 ±0.64
1.	1.8M LiAlCl ₄ /SOCl ₂ + 5% S ₂ Cl ₂	3.69	< 1 sec.	3.35	28.4	13.28 ±0.05	44.50 ±0.02
2.	1.5M LiAlCl ₄ /SO ₂ Cl ₂	3.89	3 min.	3.30	35.3	12.89 ±0.16	42.67 ±0.70
2.	1.25M LiAlCl ₄ /SO ₂ Cl ₂ + 0.25M(MEIC+AlCl ₃)	3.87	4 min.	3.23	29.9	12.73 ±0.05	41.10 ±0.16
2.	1.25M LiAlCl ₄ /SOCl ₂ + 0.25M(TMSC+AlCl ₃)	3.63	2 sec.	3.30	27.4	12.00 ±1.17	39.53 ±4.10
2.	1.25M LiAlCl ₄ /SOCl ₂ + 0.25M(MEIC+AlCl ₃)	3.62	< 1 sec.	3.32	28.5	10.29 ±0.37	34.11 ±1.29

Note: All SOCl₂ cells contained polvinyl chloride for voltage delay control.

Table 5

F Cell Temperatures at Mid-life on 2A and 7A Tests

<u>Electrolyte</u>	Mid-life Temp. (°C)	
	<u>2A</u>	<u>7A</u>
1.5M LiAlCl ₄ /SOCl ₂	29.2	55
1.5M LiGaCl ₄ /SPCl ₂	38.2	63
1.8MLiAlCl ₄ /SOCl ₂	28.8	54
1.8M LiAlCl ₄ /SOCl ₂ + 5% S ₂ Cl ₂	28.4	54
1.5M LiAlCl ₄ /SO ₂ Cl ₂	35.3	76
1.25M LiAlCl ₄ /SO ₂ Cl ₂ + 0.25M(MEIC+AlCl ₃)	29.9	(1)
1.25M LiAlCl ₄ /SO ₂ Cl ₂ + 0.25M(TMSC+AlCl ₃)	27.4	60
1.25M LiAlCl ₄ /SOCl ₂ + 0.25M(MEIC+AlCl ₃)	28.5	54

Table 6

Effect of Temperature on F Cell Capacity

<u>Test</u>	<u>Electrolyte</u>	<u>Capacity (Ah)</u>	<u>Mid-life Temperature (°C)</u>	<u>Number of Cells</u>
2A @ 21°C	1.5M LiAlCl ₄ /SOCl ₂	12.88 ± 0.42	28.4 ± 0.42	6
2A @ 54°C	1.5M LiAlCl ₄ /SOCl ₂	14.44 ± 0.10	57.7 ± 0.49	5

Table 7

Performance of F Cells With New Electrolytes

7A Discharge at 21°C

<u>Electrolyte</u>	<u>Capacity (Ah)</u>	<u>Midlife Voltage</u>	<u>Energy (Wh)</u>	<u>MidlifeTemp (°C)</u>
1.5M LiGaCl ₄ /SOCl ₂	14.56 ±0.00	3.05 ±0.03	44.41 ±0.41	61.0 ±2.8
1.8M LiAlCl ₄ /SOCl ₂	13.37 ±0.59	3.13 ±0.02	41.78 ±1.60	52.0 ±2.8
1.5M LiAlCl ₄ /SOCl ₂	12.36 ±0.15	3.12 ±0.06	38.49 ±0.38	49.0 ±2.8
1.8M LiAlCl ₄ /SOCl ₂ + 5% S ₂ Cl ₂	11.90 ±0.20	3.05 ±0.06	36.29 ±0.07	51.0 ±1.4
1.5M LiAlCl ₄ /SO ₂ Cl ₂	11.20 ±0.99	3.30 ±0.01	36.97 ±3.42	81.5 ±2.1

Note: all SOCl₂ electrolytes contain polyvinyl chloride to control voltage delay.

Table 8

Performance of F Cells With New Electrolytes

Test: 4 Weeks @ 54°C, 2A constant current discharge @ -30°C
2 cells per lot.

<u>Electrolyte</u>	<u>OCV</u>	<u>Midlife Voltage</u>	<u>Midlife T (°C)</u>	<u>Capacity (Ah)</u>
1.5M LiGaCl ₄ /SOCl ₂	3.66	2.90±.00	-9.0±1.4	5.71±1.82
1.5M LiAlCl ₄ /SOCl ₂	3.72	2.96±.01	-17.5±0.7	5.47±0.11
1.8M LiAlCl ₄ /SOCl ₂ + 5% S ₂ Cl ₂	3.74	2.93±.00	-17.0±0.0	5.25±0.43
1.8M LiAlCL ₄ /SOCl ₂	3.73	2.93±.01	-18.5±0.7	4.66±0.39
1.25M LiAlCl ₄ /SO ₂ Cl ₂ + 0.25M(MEIC+AlCl ₃)		vented on 54°C shelf		
1.25M LiAlCl ₄ /SO ₂ Cl ₂ + 0.25M(TMSC+AlCl ₃)	3.05	cell would not carry 2A, leaked on 54°C shelf.		
1.25M LiAlCL ₄ /SOCl ₂ + 0.25M(MEIC+AlCl ₃)		leaked on 54°C shelf		
1.5M LiAlCl ₄ /SO ₂ Cl ₂	3.88	cells would not carry 2A current		

Note: all SOCl₂ cells contained polyvinyl chloride for voltage delay control.

Table 9

Performance of F Cells With New Electrolytes
in Optimized Design

2A discharge at 21°C, Capacity (Ah) to 2.7V

Cathode thickness (inches):	0.028	0.041	0.053
<u>Anode thickness (inches):</u>	<u>0.012</u>	<u>0.014</u>	<u>0.018</u>
1.5M LiAlCl ₄ /SOCl ₂	13.21	11.85±.04	11.59±.13
1.5M LiGaCl ₄ /SOCl ₂	13.60±.05	11.95±.06	12.17±.06
1.8M LiAlCl ₄ /SOCl ₂	12.18±.48	11.74±.13	11.55±.19
1.8M LiAlCl ₄ /SOCl ₂ + 5% S ₂ Cl ₂	12.55±.09	10.96±.10	10.49±.08
1.5M LiAlCl ₄ /SO ₂ Cl ₂	12.25±.13	10.41±.35	(1)

(1) test board problems

Note: all SOCl₂ cells contain polyvinyl chloride for voltage delay control.

Table 10

Performance of F Cells With New Electrolytes
in Optimized Design

7A Discharge at 21°C, Capacity (Ah) to 2.7V

Cathode thickness (inches):	0.028	0.041	0.053
<u>Anode thickness (inches):</u>	<u>0.012</u>	<u>0.014</u>	<u>0.018</u>
1.5M LiGaCl ₄ /SOCl ₂	14.56±0	12.88±.01	11.66±.35
1.8M LiAlCl ₄ /SOCl ₂	13.37±.59	12.71±.15	9.56±.35
1.5M LiAlCl ₄ /SOCl ₂	12.36±.15	11.31±.15	9.00±.15
1.8M LiAlCl ₄ /SOCl ₂ + 5% S ₂ Cl ₂	11.90±.20	11.06±.00	6.83±.25
1.5M LiAlCl ₄ /SO ₂ Cl ₂	11.20±.99	9.66(1)	(1)

(1) Cell vent on test.

Note: all SOCl₂ cells contain polyvinyl chloride for voltage delay control.

Fig 1

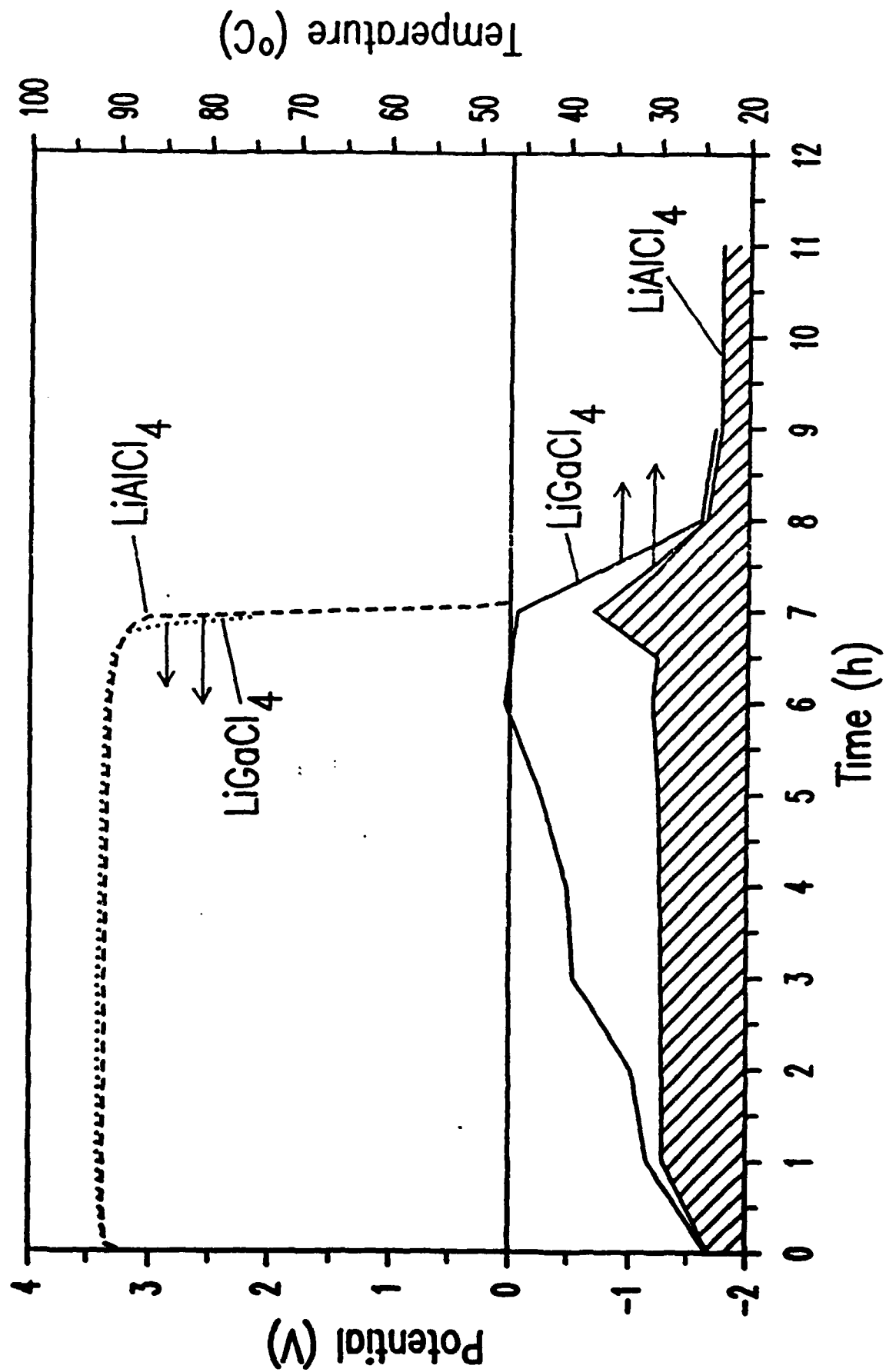


Fig 2

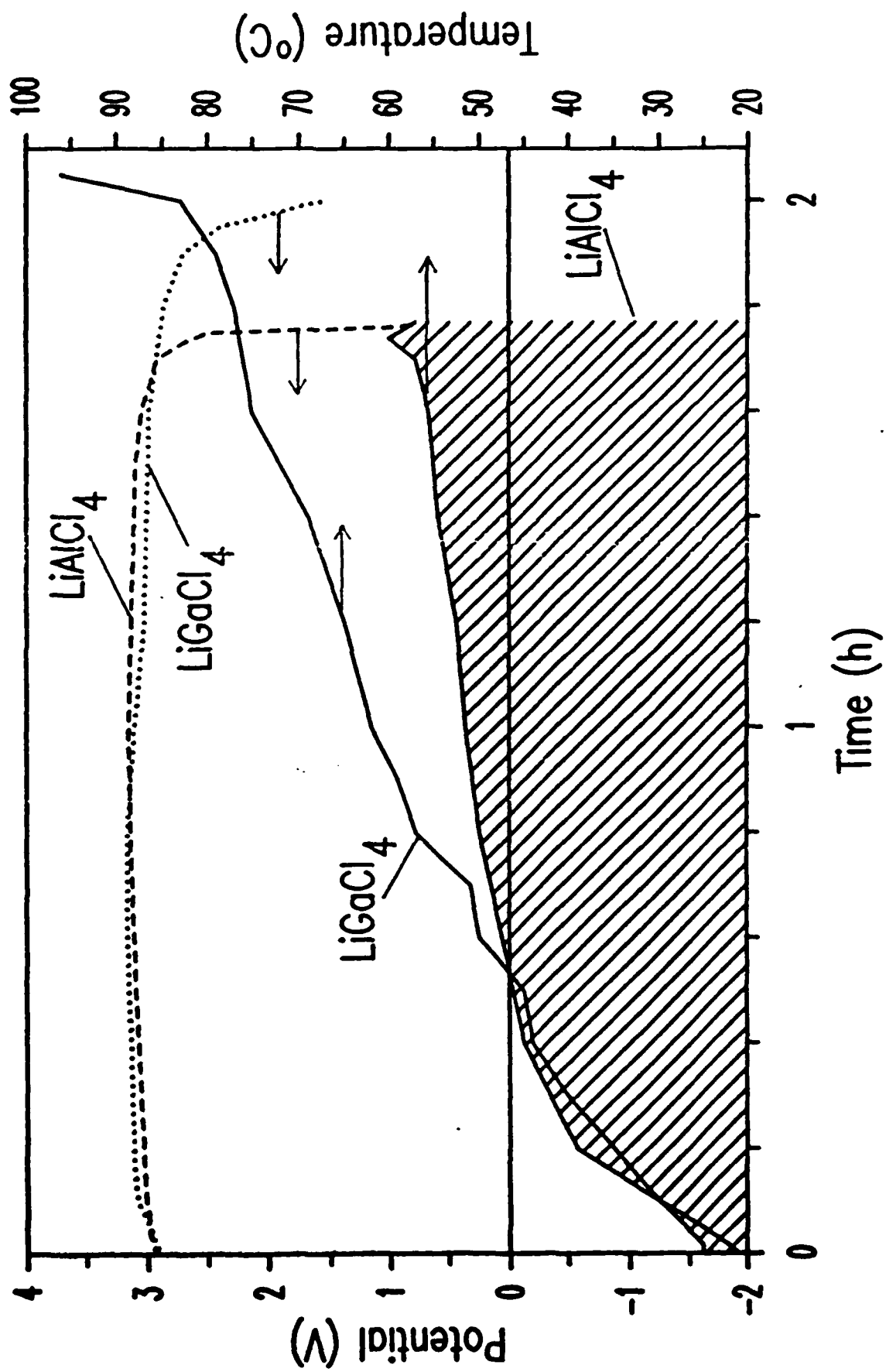


Fig 3

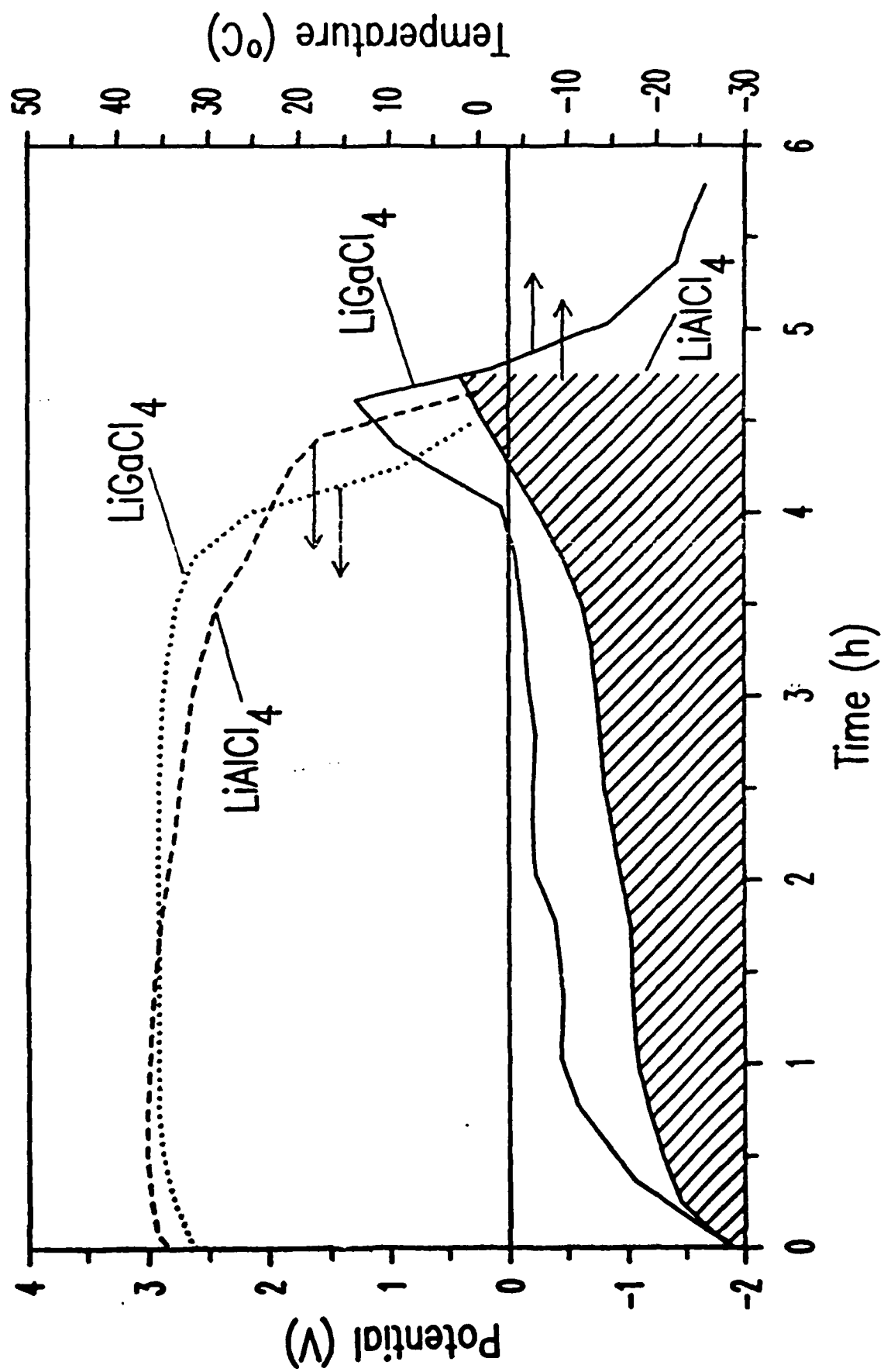


Fig 4

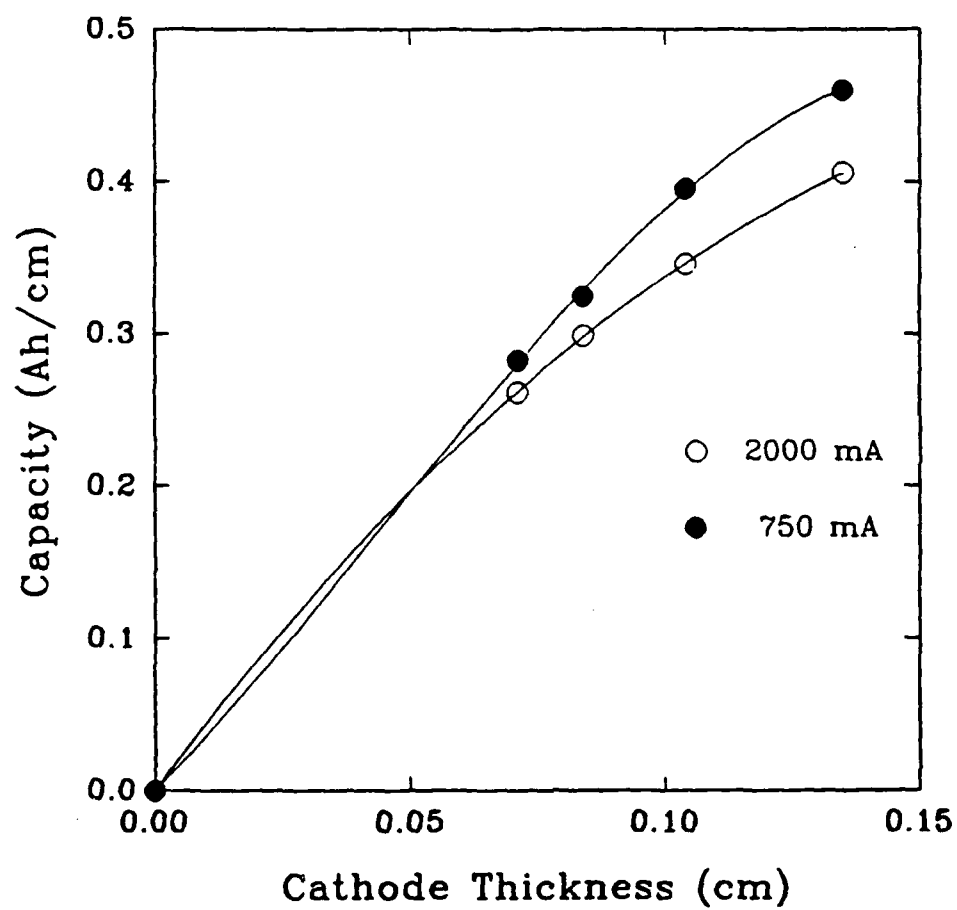


Fig 5

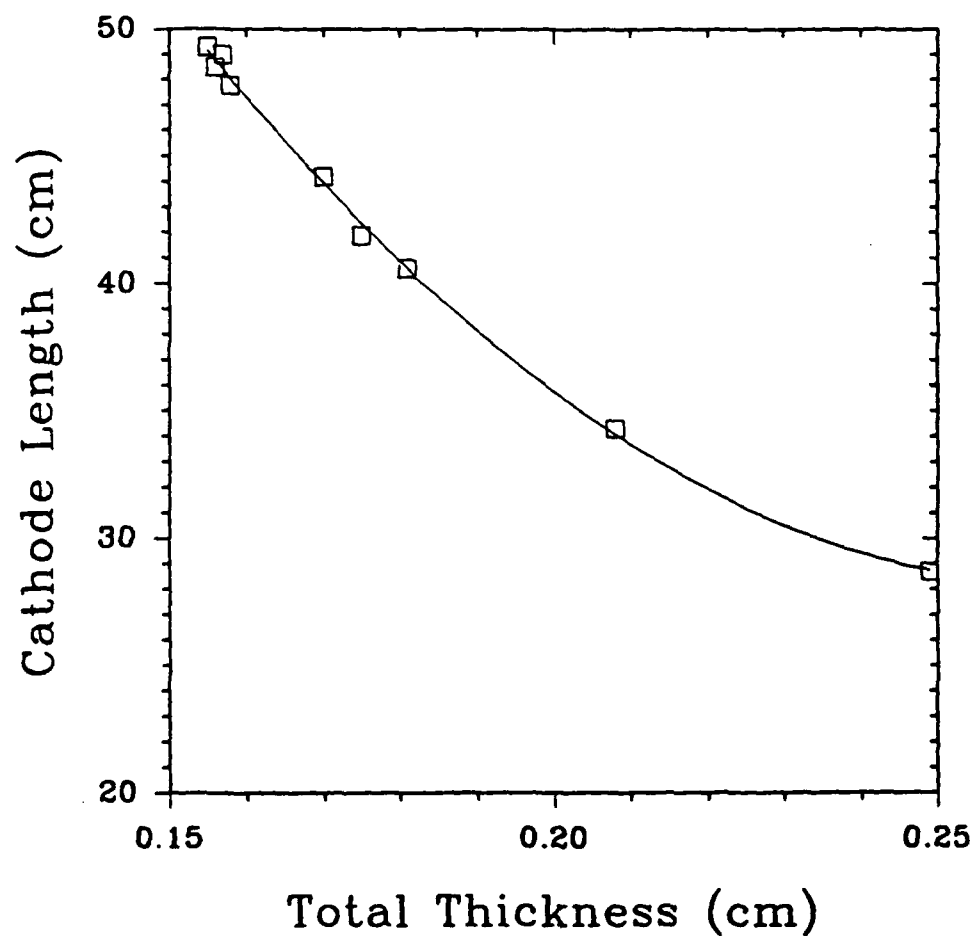
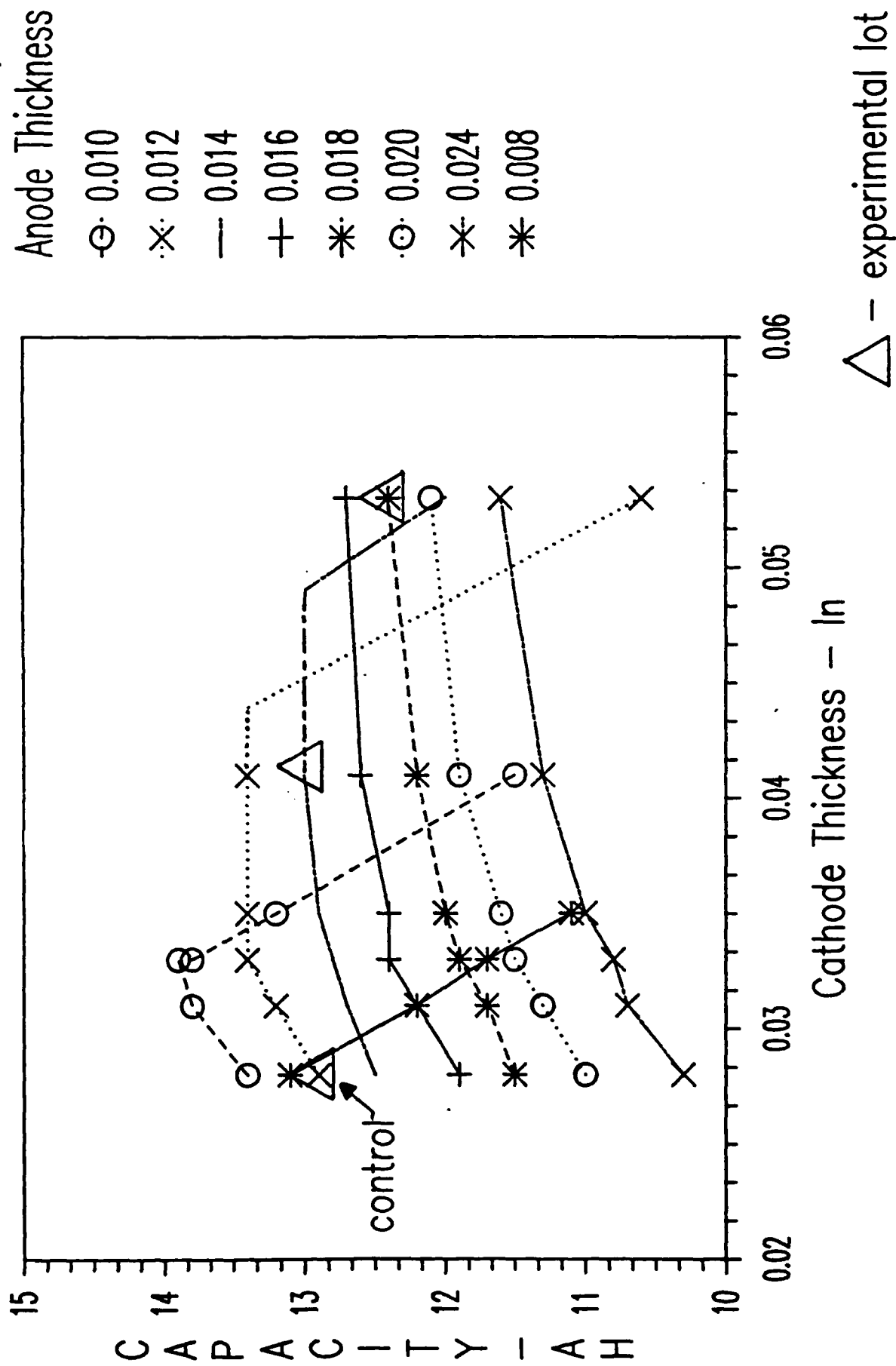


Fig. 6

Calculated Capacity of F Cells on 2A Test



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